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THE CRYSTAL STRUCTURE OF
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(U) VERMONT UNIV BURLINGTON DEPT OF CHEMISTRY
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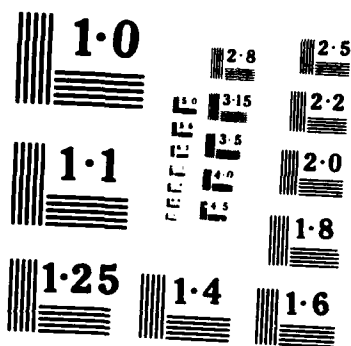
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The Crystal Structure of 2,2-Bis(Trimethylsilylamino)-
tetrachlorocyclotriphosphazene.

by

C.W. Allen, D.E. Brown, A.W. Cordes and S.L. Craig

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The Crystal Structure of 2,2-Bis(Trimethylsilylamino)
tetrachlorocyclotriphosphazene, $N_3P_3Cl_4(NHSiMe_3)_2$

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Abstract. $P_3N_3Si_2Cl_4H_{20}$, $M_r = 453.2$, monoclinic, $C2/c$, $a = 13.749(6)$, $b = 7.343(3)$, $c = 20.124(3) \text{ \AA}$, $\beta = 95.24(3)^\circ$, $V = 2023(2) \text{ \AA}^3$, $Z = 4$, $D_x = 1.49 \text{ g cm}^{-3}$, $\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$, $\mu = 9.4 \text{ cm}^{-1}$, $F(000) = 928$, $T = 293 \text{ K}$, $R = 0.049$ for 961 unique observed reflections. The phosphazene ring lies on a crystallographic 2-fold axis and is planar within $0.031(5) \text{ \AA}$. The exo P-N bond distance is $1.609(5)$ and the Si-N bond distance is $1.757(5) \text{ \AA}$ which suggests preferential nitrogen lone pair delocalization to the phosphorus atom. P-N distances in the ring alternate (from the P with the exo N atoms) from $1.617(5)$ to $1.551(5)$ to $1.591(4) \text{ \AA}$. The structural and ^{31}P nmr parameters of $2,2-N_3P_3Cl_4(NHSiMe_3)_2$ are compared to the analogous tert-butylamino derivative.

* Supplementary data available (No. , pp); H-atom coordinates, anisotropic thermal parameters. See instruction for Authors, J. Chem. Soc., Dalton Trans., 1986, Issue 1, pp. xvii - xx. Structure factors are available from the editorial office.

A-1

The π -donor interaction of exocyclic substituents with phosphorus centers in cyclophosphazenes is a topic of continuing interest and controversy. Spectroscopic evidence indicates that aryl π -donation is non-existent¹ or low² while in substituents containing lone pairs of electrons such as carbanions^{3,4} and amines⁴⁻⁶, the π donor effect is believed to be significant. In the most widely studied systems, the aminophosphazenes, the exocyclic nitrogen atoms is in a trigonal planar environment and the exocyclic phosphorus-nitrogen bonds are significantly shorter than the expected single bond distance.^{5,6} The exceptions to these generalizations are the aziridine derivatives where the amine is tetragonal and the exocyclic phosphorus-nitrogen distances are longer than those found in other systems.⁷ In this paper, we examine the effect of placing another second row acceptor center on the exocyclic nitrogen atom in 2,2-N₃P₃Cl₄(NHSiMe₃)₂ and compare the results with the previously reported structure⁸ of the carbon analog, 2,2-N₃P₃Cl₄(NHCMe₃)₂.

Experimental

Materials and Methods. Hexachlorocyclotriphosphazene (Shin Nisso Kako) was converted to 2,2-N₃P₃Cl₄(NHSiMe₃)₂⁹ (1) and 2,2-N₃P₃Cl₄(NHCMe₃)₂^{8,12} (2) by previously reported procedures. The ³¹P NMR spectra (in CDCl₃) were recorded on a Bruker WM250 spectrometer operating at 101.2 MHz and using 85% H₃PO₄ as an external reference. The spectra were recorded under conditions of broad band decoupling and chemical shifts upfield of the reference are assigned a negative sign.

X-ray Analysis of $N_3P_3Cl_4(NHSiMe_3)_2$. Crystals suitable for X-ray were obtained from CCl_4 solution. A colorless platelet of approximate dimensions $0.02 \times 0.40 \times 0.46$ mm, mounted on a glass fiber was used for data collection on an Enraf-Nonius CAD-4 diffractometer using variable speed (3 to 17 deg/min) ω - 2θ scans. D_m was not measured. The unit cell was determined from a least-squares fit of the angle data for 25 reflections with $18^\circ < 2\theta < 22^\circ$. The analytical absorption correction¹⁵ based on crystal shape varied from 0.68 to 1.00. Data was collected to $\sin \theta/\lambda$ of 0.60 - $6 \leq h \leq 0$, $-8 \leq k \leq 0$, $-23 \leq l \leq 23$. The data was collected in two shells. Three standard reflections ($-6\ 0\ 4$, $-3\ -3\ -3$, $-1\ -1\ 9$) decayed 32% over 16.2 hours of data collection; anisotropic correction was applied. 2304 reflections were measured, 1775 unique ($R_{int} = 0.02$), 814 reflections with $I < 3\sigma(I)$ were considered unobserved. The structure was solved by direct methods (Mullan 1982)¹³ and refined by full-matrix least-squares minimized $\sum w(\Delta F)^2$. Methyl hydrogen atom orientations were determined on difference maps and methyl hydrogen atoms were constrained to idealized (C-H = 0.95 Å) positions with isotropic $B = 1.2 \times B$ of the bonded carbon atom. The hydrogen atom on nitrogen was located on a difference map and was refined with a constrained isotropic thermal parameter. All non-hydrogen atoms were refined anisotropically for a total of 92 variables. The final refinement with observed data gave $R = 0.049$, $R_w = 0.062$ and $S = 1.32$, where non-Poisson $w^{-1} = (\sigma^2(I) + 0.0036 I^2)/4F^2$. Final (Δ/σ) max < 0.07 , $\Delta\rho_{max} = 0.40(6)$ and $\Delta\rho_{min} = -0.40(6)$ e⁻Å⁻³ on the final difference map. The atomic scattering factors and anomalous dispersion corrections are from the International Tables for X-ray crystallography (1974)¹⁴ and

the programs used those of the Enraf (1982) SDP package.¹⁵

Results and Discussion

The crystal and molecular structures of 1 were determined in order to ascertain the effect of the replacement of a carbon atom by a silicon atom on the exocyclic nitrogen atom in an aminocyclophosphazene. The final atomic coordinates of all unique atoms are given in Table I. Selected bond lengths and bond angles may be found in Table II and an ORTEP drawing, together with atom-numbering scheme, is shown in Figure 1. The observed molecular structure of 1 confirms the geminal configuration of the trimethylsilylamino groups which was previously predicted on a chemical basis⁹, based on the known geminal configuration of $N_3P_3Cl_4(NH_4)_2$ ¹⁰, the chemical precursor to 1. In a comparison of the structure of 1 with its tert-butylamino analog, 2,⁸ a striking similarity of structural parameters with some subtle differences is noted. In the structure of 2, a well developed hydrogen-bond network exists between an exocyclic amino hydrogen atom and an endocyclic nitrogen atom. This gives rise to two different orientations of the tert-butylamino groups. In 1, both of the trimethylsilylamino groups are in the same configuration and the closest intermolecular contacts are between the exocyclic amino nitrogen atom and N(1) of the next molecule along a two fold axis. The observed N(3) ---- N(1) distance is 3.34 Å placing it at the outer limit of N-H N hydrogen-bonds (2.8 to 3.4 Å). Hydrogen-bonding arrays of this type have been observed in other cyclophosphazene derivatives.¹¹ The N_3P_3 ring in 1 is planar within 0.031(2) Å while in 2 the N_3P_3 ring exhibits a slight boat conformation. The exocyclic nitrogen atoms in 1 are in the center of a trigonal planar array.

The phosphorus-nitrogen bond lengths and angles in 1 and 2 are nearly identical. The particular points of interest are the exocyclic phosphorus-nitrogen bond lengths (1.609(5) in 1 and a mean distance of 1.609 in 2) and the exocyclic NPN angles (105.9(4) in 1 and 104.1(8), 103.9(6) for the two independent molecules of 2). It has been proposed that there exists a relationship between exocyclic OPN bond angles and ^{31}P NMR chemical shifts in cyclophosphazenes.¹⁶ The ^{31}P NMR data for 1 and 2 are given in Table III and one indeed finds a significant chemical shift difference for the $\text{=P(NHMMe}_3\text{)}$ ($\text{M}=\text{C, Si}$) centers, but any attempted correlation with the exocyclic NPN angle should be viewed with caution since all these bond angles in 1 and 2 lie within three standard deviations and hence must be considered statistically indistinguishable.

The range of bond lengths in unconstrained silicon-nitrogen fragments is 1.688–1.759 Å,¹⁷ so the value observed for 1 (1.757(5)) is amongst the longest of these bonds. An analogous situation occurs in disilylamino centers where one of the silicon atoms has silicon-fluorine bonds. In these cases, the silicon-nitrogen bond to the fluorinated silicon center is short and the remaining silicon-nitrogen bond is longer.^{18,19} Since the exocyclic phosphorus-nitrogen distances in 1 and 2 are equivalent, the delocalization of the exocyclic nitrogen lone pair of electrons is equivalent in each case. Although extended Hückel calculations support the transfer of nitrogen lone pair electron density to silicon 3d orbitals in $\text{NMe}_2(\text{SiMe}_3)$,²⁰ the strongly electron withdrawing P(V) center in 1 is a better π acceptor than the Si(IV) center and the long silicon-nitrogen bond lengths reflects a decreased transfer of π electron den-

sity to the silicon atom. Competition for nitrogen lone electron pairs between phosphorus and acyl centers have also been investigated by structural studies.²¹ A rough correlation between short silicon-nitrogen bond lengths and increased percentage s character has been noted.¹⁷ If this effect were operative in 1, the more electronegative P(V) would direct more p character to the P(2)--N(3) bond hence causing an increased s character in the N(3)-Si bond.²² Since a long, rather than short, silicon-nitrogen bond is observed it appears reasonable to ascribe the variations in exocyclic nitrogen lone pair delocalization described above as being reasonable for the long silicon-nitrogen bond length.

Acknowledgements

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Table I. Positional Parameters^a

Atom	x	y	z	U (Å ²)
Cl(1)	0.0869(1)	0.2885(3)	0.6274(1)	4.4(1)
Cl(2)	0.2115(1)	0.2814(3)	0.7526(1)	4.4(1)
P(1)	0.0822(1)	0.1926(2)	0.7176(4)	1.1(1)
P(2)	0.000	-0.1423(3)	0.750	1.1(1)
Si	-0.0770(2)	-0.2355(3)	0.6066(19)	3.1(1)
N(1)	0.000	0.305(1)	0.750	3.4(1)
N(2)	0.0782(3)	-0.0185(7)	0.7151(3)	2.6(1)
N(3)	-0.0483(4)	-0.2743(7)	0.6923(2)	3.0(1)
C(1)	0.0371(6)	-0.226(1)	0.5636(3)	5.1(2)
C(2)	-0.1455(6)	-0.020(1)	0.5952(4)	4.7(2)
C(3)	-0.1557(6)	-0.431(1)	0.5781(4)	5.5(2)

a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3) * [a^2 * B(1,1) + b^2 * B(2,2) + c^2 * B(3,3) + ac(\cos \beta) * B(1,3)]$; atoms marked with an asterisk were refined isotropically.

Table II. Bond Distances(Å) and Angles (deg) for 2,2-N₃P₃Cl₄(NHSiMe₃)₂^a

P(1)-Si	P(1)	2.011(2)	Si	N(3)	1.757(5)	
P(1)-Si	P(1)	1.997(2)	Si	C(1)	1.861(7)	
P(1)-N(1)	N(1)	1.591(4)	Si	C(2)	1.848(7)	
P(1)-N(2)	N(2)	1.551(5)	Si	C(3)	1.856(7)	
P(2)-N(2)	N(2)	1.617(5)	N(3)	H(10)	0.75(6)	
P(2)-N(3)	N(3)	1.609(5)				
P(1)-P(2)	C(1)	99.3(1)	N(3)	Si	C(2)	109.1(3)
P(1)-P(2)	N(1)	106.9(2)	N(3)	Si	C(3)	104.5(3)
P(1)-P(2)	N(2)	109.2(2)	C(1)	Si	C(2)	110.6(3)
P(1)-P(2)	N(1)	107.5(2)	C(1)	Si	C(3)	112.2(3)
P(1)-P(2)	N(2)	111.4(2)	C(2)	Si	C(3)	110.4(4)
N(1)-P(1)	N(2)	120.4(3)	P(1)	N(1)	P(1)'	117.4(4)
N(2)-P(1)	N(2)'	111.6(3)	P(1)	N(2)	P(2)	125.0(3)
N(2)-P(1)	N(3)	105.8(2)	P(2)	N(3)	Si	130.7(3)
N(2)-P(1)	N(3)'	113.9(3)	P(2)	N(3)	H(10)	115.(5)
N(3)-P(1)	N(3)'	108.9(4)	Si	N(3)	H(10)	114.(5)
N(3)-P(2)	C(1)	109.8(3)				

a. Numbers in parentheses are estimated standard deviations in the least significant digits.

Table III. Selected ^{31}P NMR data for compounds 1 and 2.

<u>Compound</u>	<u>$\delta_{\text{P}}(\text{NHMe}_3)^{\text{a}}$</u>	<u>$\delta_{\text{PCl}_2}^{\text{a}}$</u>	<u>$^2J_{\text{PP}}^{\text{b}}$</u>
1	9.4	22.1	50.9
2	2.3	19.6	44.7

a. in ppm b. in Hz

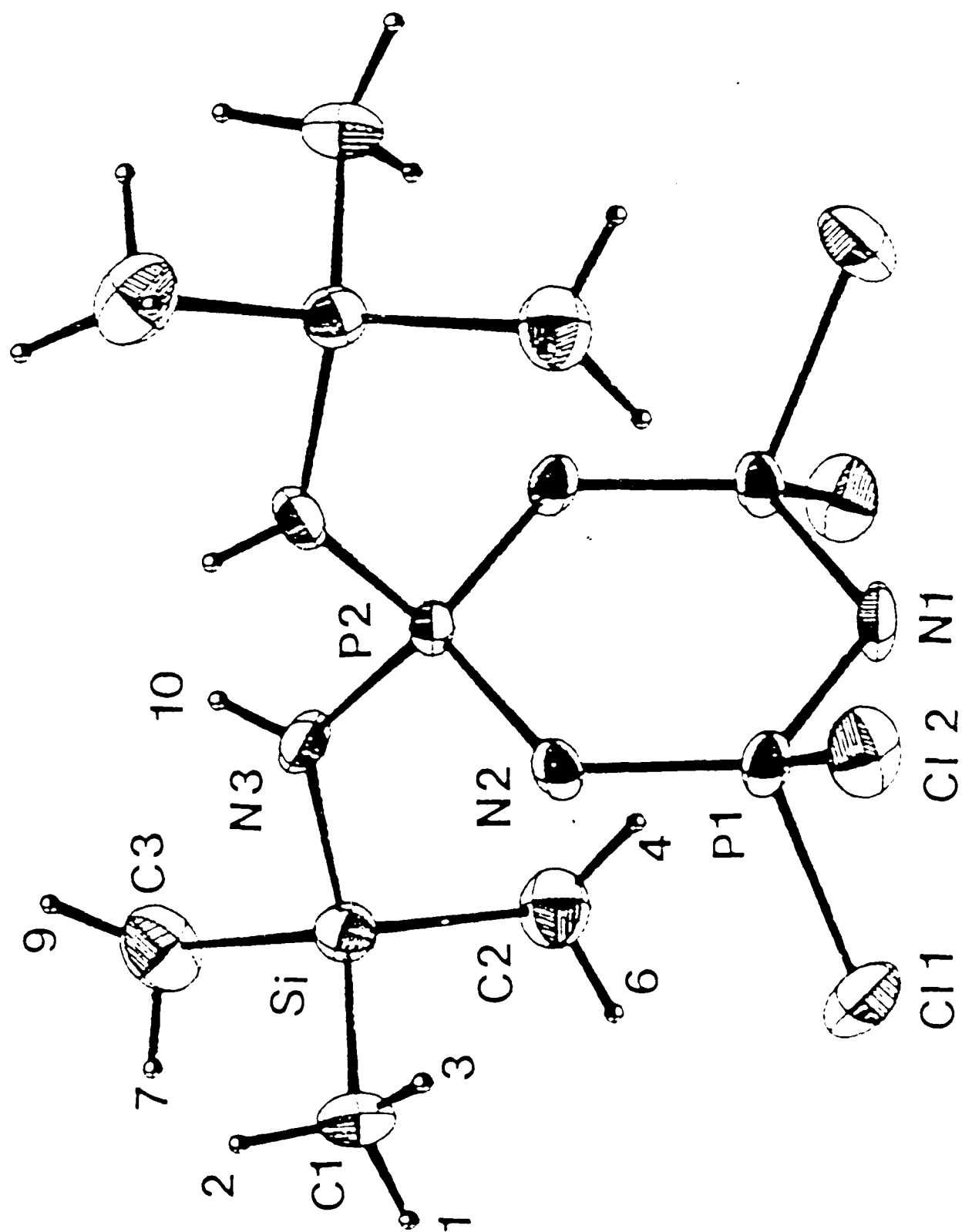


Figure. View of $\text{N}_3\text{P}_3\text{Cl}_4[\text{NHSi}(\text{CH}_3)_3]_2$ with the atomic numbering scheme.

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